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Probing the interactions of phenol with oxygenated functional groups on curved fullerene-like sheets in activated carbon

Chun-Yang Yin, [a,§,*] Man-Fai Ng, [b,§,*] Bee-Min Goh [c], Martin Saunders, [d] Nick Hill, [a] Zhong-Tao Jiang, [e] Juan Balach, [f] Mohanad El-Harbawi, [g]

[a] *School of Science and Engineering, Teesside University, Borough Road, Middlesbrough, TS1 3BA, United Kingdom*

[b] *Institute of High Performance Computing, Agency for Science, Technology and Research, 1 Fusionopolis Way, #16-16 Connexis, Singapore 138632, Singapore*

[c] *School of Chemical Engineering and Advanced Materials, Newcastle University, NE1 7RU, United Kingdom*

[d] *Centre for Microscopy, Characterisation and Analysis (CMCA), The University of Western Australia (M010), 35 Stirling Highway, Crawley WA 6009, Australia*

[e] *Surface Analysis and Materials Engineering Research Group, School of Engineering & Information Technology, Murdoch University, Murdoch, Western Australia 6150, Australia*

[f] *Leibniz Institute for Solid State and Materials Research (IFW) Dresden, Institute for Complex Materials, Helmholtzstraße 20, D-01069 Dresden, Germany*

[g] *Chemical Engineering Department, King Saud University, Riyadh 11421, Saudi Arabia*

[§]These authors contributed equally to this work. *Corresponding authors Tel.: +44 164273 8523. Email: c.yin@tees.ac.uk (C.-Y.Y.); ngmf@ihpc.a-star.edu.sg (M.-F.N.)

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ABSTRACT

The mechanism(s) of interactions of phenol with oxygenated functional groups (OH, COO and COOH) in nanopores of activated carbon (AC) is a contentious issue among researchers. This mechanism is of particular interest because a better understanding of the role of such groups in nanopores would essentially translate to advances in AC production and use, especially in regard to the treatment of organic-based wastewaters. We therefore attempt to shed more light on the subject by employing density functional theory (DFT) calculations in which fullerene-like models integrating convex or concave structure, which simulate the eclectic porous structures on AC surface, are adopted. TEM analysis, EDS mapping and Boehm titration are also conducted on actual phenol-adsorbed AC. Our results suggest the widely-reported phenomenon of decreased phenol uptake on AC due to increased concentration of oxygenated functional groups is possibly attributed to the increased presence of the latter on the convex side of the curved carbon sheets. Such a system effectively inhibits phenol from getting direct contact with the carbon sheet, thus constraining any available π-π interaction, while the effect of groups acting on the concave part of the curved sheet does not impart the same detriment.

Keywords: Activated carbon; density functional theory; transmission electron microscopy; phenol adsorption; oxygenated functional groups

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1. INTRODUCTION

Activated carbon (AC) is an effective adsorbent for removal of a wide variety of pollutants dissolved in aqueous media, or from gaseous environments, due to its exceptionally high surface area, well-developed internal micro- and mesoporous structure, as well as the presence of a wide spectrum of surface functional groups[1]. It is an established fact that ACs are generally geared towards removal of organic adsorbates[2]. One such prominent organic contaminant comes in the form of phenol-based compounds. These compounds are by-products from oil refinery wastewaters, coal gasification sites and petrochemical units and are toxic and carcinogenic even at very low concentrations[3]. It is important to note that the mechanism of phenol adsorption is of particular interest because a better understanding of selective adsorption would essentially translate to advances in AC preparation, design and selection.

It is a widely established notion that the presence of oxygenated functional groups within the AC pores effectively reduces the adsorption of phenol at small equilibrium concentrations[4,5]. There were essentially two major postulates that elucidated this phenomenon whereby the first postulate described the reduction in the energy of π-π interactions between the carbon matrix and benzene ring of the phenol molecule, which was attributed to the changes in the electron density of carbon after the introduction of oxygenated functional groups[6,7]. The other competing postulate concerned a more physical aspect described by Coughlin and Ezra[8] who suggested that these oxygenated functional groups enhanced the affinity of water to carbon, resulting in solvent molecules effectively blocking some of the micropores from phenol molecules. A concerted effort in resolving these fundamental issues will therefore assist in enhancing selective adsorption, which ultimately improves actual AC industrial treatment capacities.

There is a recent suggestion that microporous carbon may exhibit a fullerene-like structure[9] with the possible existence of a pentagonal arrangement of carbon rings in AC[10]. These are

fullerene-related building blocks consisting of graphene sheet fragments with localized curvatures caused by randomly arranged five- and/or seven-fold rings in the hexagonal network which are essentially "topological defects" of graphene sheets[11,12]. These defects were first reported by Stone and Wales in 1986[13] and they are important in sp^2-bonded carbon materials, playing a significant role in the formation, transformation, fracture and embrittlement of carbon nanostructures[14]. Terzyk and co-researchers[5] conducted molecular dynamics simulation studies and reported that an optimal microporous carbon for phenol adsorption should possess micropores with diameters around 0.6 nm. They subsequently continued this relevant investigation recently whereby they compared the behaviour of phenol in realistic pores with ideal slit-like pores[15]. Cam and co-researchers[16] recently reported theoretical findings on adsorption of phenol on AC functionalized with several oxygenated functional groups (OH, CHO, or COOH). To further shed light on the possibilities of the abovementioned two postulates, we conduct density functional theory (DFT) calculations and simulations by using fullerene-like models incorporating curved carbon sheet structures, which collectively resemble the eclectic porous structures on ACs. Specifically, we are focusing our attention on the likelihood of phenol molecule adsorption on either the AC carbon sheet surface or the oxygenated surface functional groups. To the best of our knowledge, such an investigation was not previously reported. We also attempt to simulate a particular adsorption condition that reflects the actual experimental amount of oxygenated functional groups in the AC as determined using the quintessential Boehm titration technique.

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2. EXPERIMENTAL METHODS

Granular AC (CarbSorb 40) was obtained from Chemviron Carbon Ltd. For the batch adsorption process, 2 g of the AC was placed in an Erlenmeyer flask and 50 mL of phenol solution (1000 ppm) was added and stirred using a magnet for 8 hours. The solution was subsequently filtered and the AC washed with deionized water and dried in an oven at 50 ºC for 16 hours. To establish the amount of oxygenated functional groups present in the AC, Boehm titration was performed[17]. One gram of virgin AC was placed into a reaction vessel with 50 mL of 0.05 N solutions of HCl, NaOH, $NaHCO_3$ and Na_2CO_3. Each reaction vessel was sealed and magnetically stirred for 24 hours at 25°C and then filtered. A total of 5 mL of each filtrate sample was titrated with either HCl (0.05 N) for the bases or NaOH (0.05 N) for the acid. The amount of functional groups was established based on the assumption that NaOH neutralises carboxylic, phenolic and lactonic groups, Na_2CO_3 neutralises carboxylic and lactonic groups, and $NaHCO_3$ neutralises only carboxylic groups. The quantity of basic sites was calculated from the amount of HCl that was neutralised.

The samples were prepared for microscopy analysis by gently crushing a small piece of the dry sample between clean glass slides and then placing a continuous carbon-film covered copper TEM grid on top of the crushed material. An FEI Titan G2 80-200 TEM/STEM operating at 200 kV and equipped with a Gatan Ultrascan US1000 CCD camera, Gatan Enfinium ER electron spectrometer, and Super-X energy dispersive X-ray spectroscopy (EDS) system was used for all imaging as well as elemental analysis, respectively. Nitrogen physisorption measurements were carried out at 77 K using a Quantachrome Quadrasorb SI instrument and the data analysis was performed using the Quantachrome QuadraWin software (Version 5.05). Prior to measurement, the activated carbon sample was degassed under dynamic vacuum at 423 K for 20 h.

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3. COMPUTATIONAL METHOD

In order to discover the adsorption trend and seek a possible strategy to enhance the adsorption process, we conducted density functional theory (DFT) calculations to examine the molecular interactions between phenol and the AC surface. The model of the phenol molecule (C_6H_5OH) is shown in Figure 1. To model the surface of AC, we adopted fullerene-like models incorporating concave surface structure ("the pore on AC"), as we have shown in our previous study[18] that molecular adsorption is more effective on the concave surface of fullerene. Illustration of the surface of AC with various oxygenated functional groups (OH, COO and COOH) at various positions (edge and basal plane) is shown in Figure 1.

Geometry optimizations were performed using the wB97XD density functional[19] implemented in the Gaussian 09 suite of programs[20]. The selected functional included empirical dispersion terms, which account for the non-local interactions such as van der Waal's (vdW) interactions between the adsorbate and surface. By including vdW terms in DFT calculations, the calculated inter-distance between adsorbate and surface would be improved compared to experimental data, and thus a better model could be achieved. For the calculated energy, the trend predicated by DFT remains reliable and gives a qualitative comparison to experiments. The 6-31G(d,p) basis sets were chosen (see Electronic Supplementary Information) and used for H, C and O atoms[21]. The program's default values were used for self-consistency-field (SCF), energy and forces convergent thresholds. Zero-point energy corrections obtained from vibrational frequency calculations are included in the adsorption energy calculations. For simulation of the solvent effect of water, the polarization continuum model (PCM)[22] was used. Basis set superposition error (BSSE) is calculated based on the structures optimized in solvent.

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4. RESULTS AND DISCUSSION

To mimic the actual adsorption condition by determining the amount of oxygenated functional groups present in a commercial (virgin) AC, Boehm titration was conducted in addition to phenol adsorption. These experimental results were used as a case study (basis) for subsequent DFT studies. It was discovered that the amounts of carboxylic and phenolic groups on AC were 0.01 and 0.02 mmol/g, respectively, with approximately 25 mg of phenol adsorbed per gram of AC. Figure 2a shows the High Angle Annular Dark Field (HAADF) and EDS oxygen mapping images of virgin AC and phenol-adsorbed AC as well as the nitrogen physisorption isotherm and pore size distribution of the virgin AC. The HAADF images indicate marginal contrast in the virgin and phenol-adsorbed AC due to very little mass/density variation. This is because HAADF images are sensitive to the mass of the specimen, with the intensity approximately proportional to the squared atomic number (Z^2) of the scattering element[23]. The surface textural characteristics of the virgin AC were characterized by nitrogen physisorption experiments (Figure 1). As shown in Figure 2b, the isotherm exhibits a rapid nitrogen uptake at low relative pressure ($p/p_0 < 0.1$) and the typical type I adsorption behavior, which is characteristic for microporous materials[24]. The isotherm also displays a gradual nitrogen adsorption at relatively high pressure ($p/p_0 > 0.4$) and a slight hysteresis loop, indicating the presence of some mesopores in the virgin AC. The specific surface area derived by the Brunauer–Emmett–Teller (BET) method and the total pore volume were calculated to be 890 m^2 g^{-1} and 0.425 cm^3 g^{-1}, respectively. As shown in Figure 2b, the pore size distribution displays two narrow micropore sizes at 0.70 and 1.45 nm, while a third dimmed peak appears about 3.2 nm. The microporosity of the AC contributes to the specific surface area of 749 m^2 g^{-1} (84% of the total surface area) and of 0.330 cm^3 g^{-1} to the micropore volume (78% of the total pore volume).

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For the DFT study, the optimized adsorption positions of phenol adsorbed on AC surfaces with OH, COO or COOH (each surface contains 2 groups on either the convex plane or edge) are shown in Figures 3 and 4. Figure 3 shows the optimized adsorption positions of phenol as interacted with both the carbon sheet and functional groups as a whole integrated system whereby Figure 4 shows the optimized adsorption positions of phenol that directly interacts with the functional groups. For comparison, phenol adsorption on virgin (pristine) AC is also simulated. The adsorption energy (E_{ad}) is calculated using the formula:

$$E_{ad} = E_{(Phenol\ on\ AC)} - (E_{Phenol} + E_{AC}) \quad (1)$$

where $E_{(Phenol\ on\ AC)}$, E_{Phenol} and E_{AC} are the total energies of the optimized phenol on AC, the optimized phenol molecule and the optimized isolated AC, respectively. The calculated adsorption energy values are of ΔH at zero Kelvin because the total electronic energy ΔE is corrected by zero-point energy. More negative adsorption energy indicates more favourable adsorption and stronger interactions.

We also evaluate the effects of basis set superposition error (BSSE) on the adsorption energies. Since BSSE cannot be calculated within solvent environment as the functionality is not supported by the software, we obtain BSSE from gas phase calculation using the structures optimized in solvent, and then use it as approximate corrections to the results simulated with solvent. The calculated phenol adsorption energies on various AC concave surfaces in water environment with and without BSSE corrections are summarized in Table 1. The BSSE corrected energies are less negative and the trend is generally consistent to the results without the corrections. As the BSSE is just an approximate correction (as it is obtained from gas phase calculation) in the present study, our discussion below will be based on the results without the BSSE corrections.

When phenol is adsorbed on the surface of AC, the main interaction between them is the π-π stacking interaction, because the plane of phenol lies in parallel with the AC sheet. In general, the adsorption of phenol is thermodynamically favourable as indicated by the negative adsorption energy. A previous study has shown that positive adsorption energy will be obtained if vdW corrections are not included in DFT calculations[16].

We first look at virgin AC in Condition "**1**". The adsorption energy is about -25 kcal/mol, which is manifested purely by a π-π stacking interaction. When compared to Conditions "**8**", "**9**" and "**10**", the adsorption energies of phenol directly on the functional groups are determined to be relatively less favourable. In the case of COOH, the main interaction is hydrogen bonding as the hydroxyl hydrogen atom in phenol interacts directly with the carbonyl oxygen atom. Whereas in the case of OH, the ring part of phenol interacts directly with the hydrogen atom of the OH group which carries δ+ charge. Condition "**10**" in Figure 4 refers to the case of mixed functional groups with a ratio of COOH:OH=1:2 which is equivalent to the concentration ratio obtained via our conducted Boehm titration. In Conditions "**8**", "**9**" and "**10**", there is virtually no effective π-π interaction between phenol and the carbon sheet, and the overall phenol-AC interactions are weakened. In regard to direct phenol interaction with OH, the adsorption energy is reduced by as much as 58% as compared to that on virgin AC (Table 1). Nevertheless, the adsorption of phenol on these functional groups remains thermodynamically favourable as the adsorption energy remains negative. Hydrogen bonding should also take place between water molecule and the functional groups, and the hydrogen bond strength should be similar to that of phenol. In such a scenario, when a water molecule forms hydrogen bonding with the functional groups, phenol could form hydrogen bonding with the attached water molecule - it will keep the phenol further away from AC and further weaken the π-π interactions. Consequently, the phenol uptake will be further decreased. Overall, the calculated results suggest that phenol uptake on AC decreases with increasing concentration of the functional groups on the carbon sheets, which

is in agreement with the conventional notion and consistent with previous experimental investigations[5].

A special case is observed: by taking the virgin AC as the reference, the AC surfaces with oxygenated functional groups exhibit marginally stronger adsorption to phenol (on the opposite side of AC to the functional groups) for Conditions "**2**" to "**6**" (2 groups per AC) regardless of the position of the groups, i.e. on basal plane or at the edge. The functional group contains highly electronegative oxygen atoms, which can induce a net dipole on the groups, and the part of the groups carrying δ+ charge attracts the electron cloud of the ring part of phenol. Although the enhancement is just < 0.45 kcal/mol (< 2 %), by increasing the concentration of the functional groups on AC, the enhanced adsorptive strength will become much more significant. We take the AC-COOH surface as an example. We doubled the numbers of functional groups to 4 on the surface (4 COOH groups per AC surface, Condition "**7**"). We find that the adsorption energy of phenol on this surface increases by 34 % as compared to the case of just 2 % increment with 2 COOH per AC (Table 1). We show here there is the possibility of theoretical enhancement of phenol adsorption on AC with the slight increase in the amount of the functional groups.

Our result essentially implies that the phenomenon of decreased phenol uptake on AC due to increased concentration of oxygenated functional groups is perhaps attributed to a direct "shielding" effect rendered by the groups (Conditions "**8**", "**9**" and "**10**"). Explicitly, the functional groups shield (or prevent) the phenol from getting direct contact with the carbon sheet, thus constraining any available π-π interaction. At this point, it is important to note that water molecules compete directly with phenol molecules to infiltrate the micropores. Indeed, such a "shielding" effect would be similar to the micropore blocking effect suggested by Coughlin and Ezra[8]. All in all, our observation does appear to support the postulate by Coughlin and Ezra[8] though in any case, oxygenated groups will definitely distort the electron density on

the AC carbon sheet. Our theoretical results also suggest that phenol adsorption might be favourable if phenol could gain access to the 'opposite' (concave) side of the heavily groups-populated convex side as illustrated by Condition "**7**".

5. CONCLUSIONS

By employing a combination of electron microscopy and DFT simulations, we have provided previously unreported insights into the optimized adsorption positions of phenol as interacted with both the carbon sheet/functional groups as a whole integrated system and those which directly interact with the functional groups. Our adsorption energy and modelling analyses reveal an interesting observation; the phenomenon of reduced phenol uptake on AC due to increased concentration of oxygenated functional groups is possibly attributed to a direct "shielding" effect rendered by the groups (in our case, COOH and OH). As such, our findings suggest the notion that COOH and OH prohibit phenol from getting direct contact with the carbon sheet, thus limiting any available π-π interaction. Alternatively, it should be noted that if the oxygenated functional groups were positioned in such a way which did not block the passage of phenol infiltration and direct contact (π-π) with the curved surface could be prominently initiated, the presence of the groups would not be detrimental to the phenol-AC adsorption process. In conclusion, our findings could potentially facilitate the design and production of bespoke AC aimed at optimizing removal of phenolic-based contaminants.

6. SUPPORTING INFORMATION

Illustration of optimized phenol adsorption process for Condition "**10**" in animated movie format and comparison of the effects of basis sets: 6-31G(d,p) and 6-311G** (Table S1).

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Table 1. Calculated adsorption energies of phenol on curved carbon sheet with different surface functional group(s). Solvent effect is simulated using water. Numbers in parentheses show BSSE corrected adsorption energies. Note that the BSSE is obtained from gas phase calculation of phenol adsorbed systems.

	Phenol Adsorption Site	Adsorption Energy in Water (kcal/mol)	% Change of Adsorption Energy with respect to Virgin Carbon Sheet
1	Virgin carbon sheet	-25.48 (-21.05)	0 (0)
2	Carbon sheet with 2×COOH on plane	-25.93 (-21.32)	+1.79 (+1.30)
3	Carbon sheet with 2×OH on plane	-25.72 (-21.07)	+0.94 (+0.11)
4	Carbon sheet with 2×COOH on edge	-25.58 (-21.18)	+0.40 (+0.62)
5	Carbon sheet with 2×OH on edge	-25.53 (-21.12)	+0.22 (+0.33)
6	Carbon sheet with 2×COO on edge	-25.87 (-21.46)	+1.55 (+1.97)
7	Carbon sheet with 4×COOH on plane	-34.29 (-28.67)	+34.58 (+36.21)
8	COOH on carbon sheet	-17.93 (-13.47)	-29.61 (-36.02)
9	OH on carbon sheet	-10.59 (-8.20)	-58.44 (-61.02)
10	COOH/OH on carbon sheet	-22.56 (-17.07)	-11.46 (-18.88)

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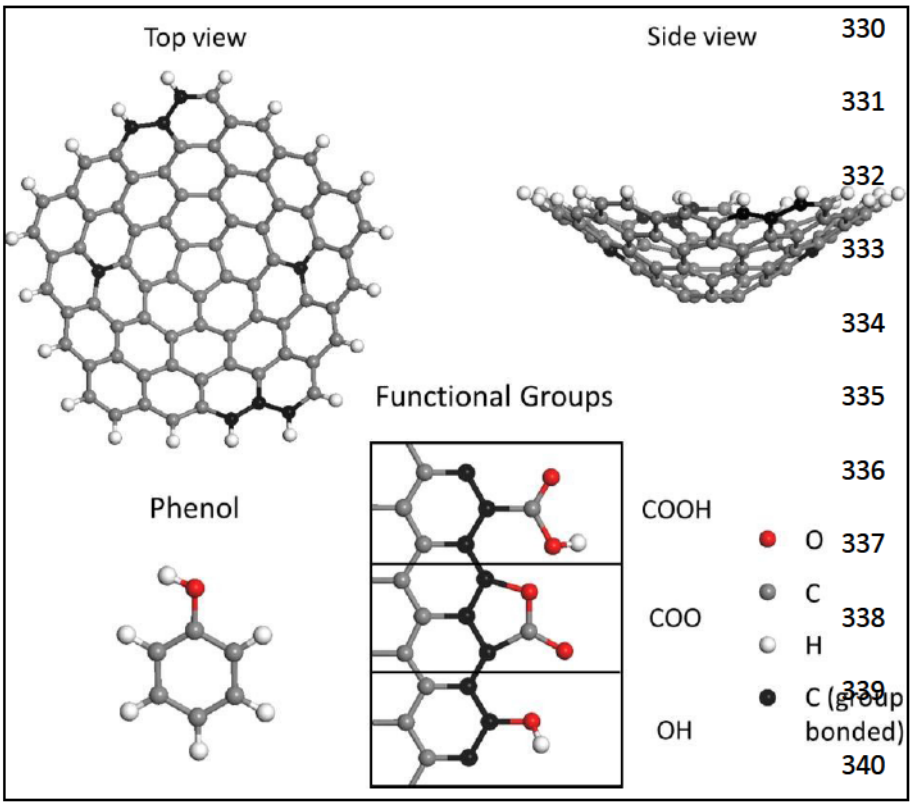

Figure 1. Structures of curved AC sheet model with a pentagonal carbon atom arrangement in the middle, phenol molecule and the functional groups: carboxylic (COOH), lactone (COO) and phenol (OH). The black carbon atoms on the AC sheet indicate the positions where the functional groups are bonded.

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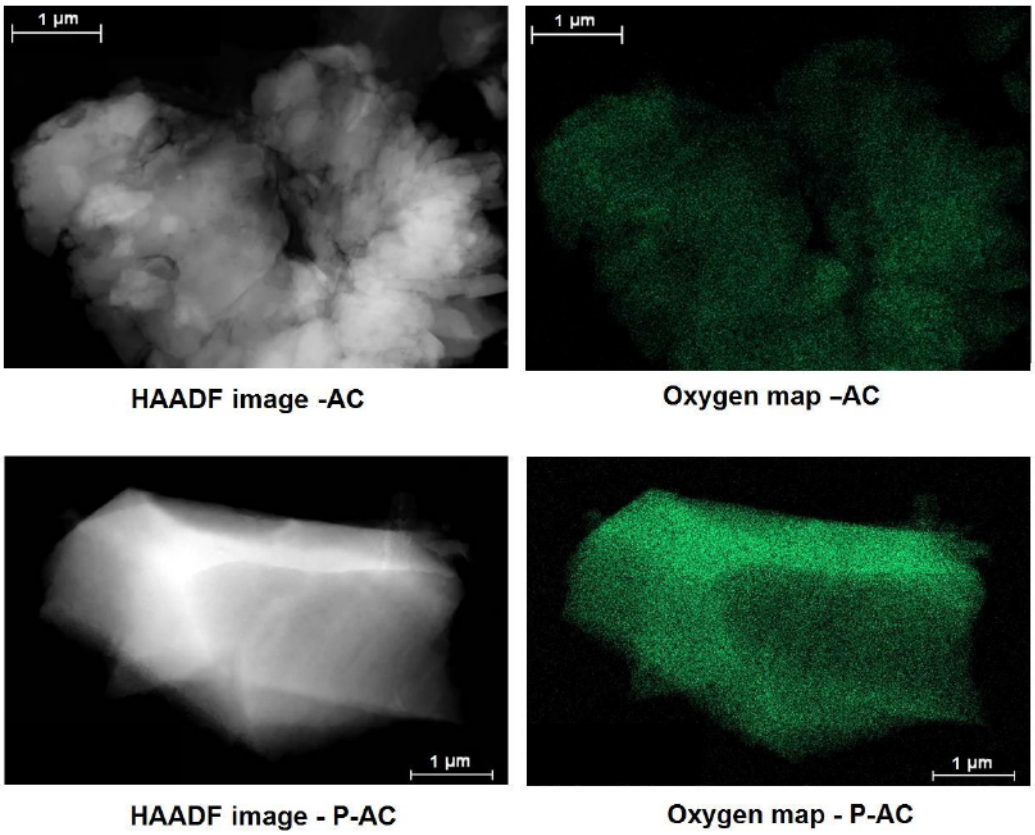
(a)



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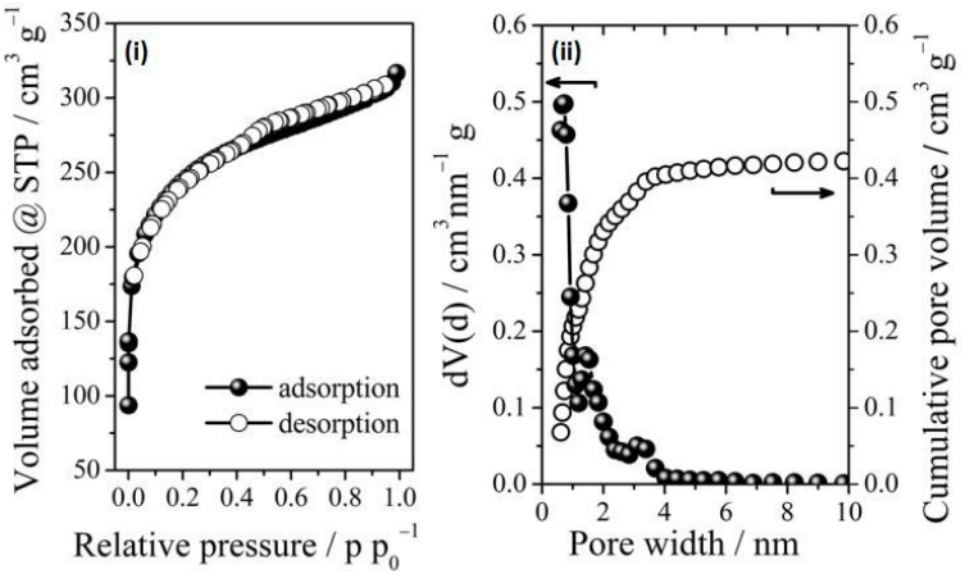

Figure 2. (a) HAADF and EDS oxygen mapping images of virgin AC and phenol-adsorbed AC (P-AC); (b-i) Nitrogen physisorption isotherm of the activated carbon and (b-ii) pore size distribution obtained by employing the QSDFT equilibrium model.

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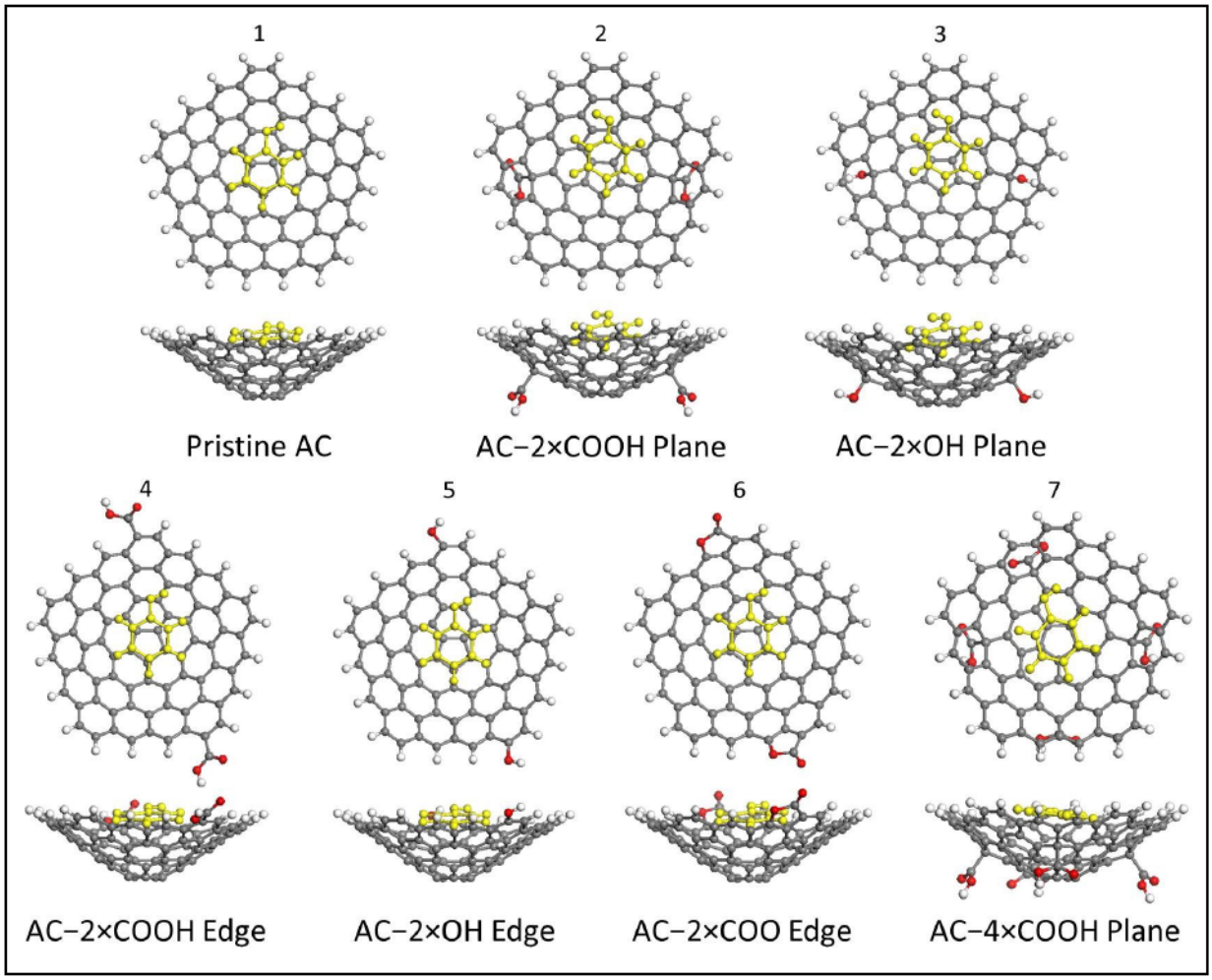

Figure 3. Optimized adsorption positions (top and side views) of phenol as interacted with both the carbon sheet and functional groups (COOH, COO and OH) as a whole integrated system. Phenol molecules are highlighted with yellow colour. 'Plane' and 'Edge' indicate the positions the functional groups (on basal plane and at the edge).

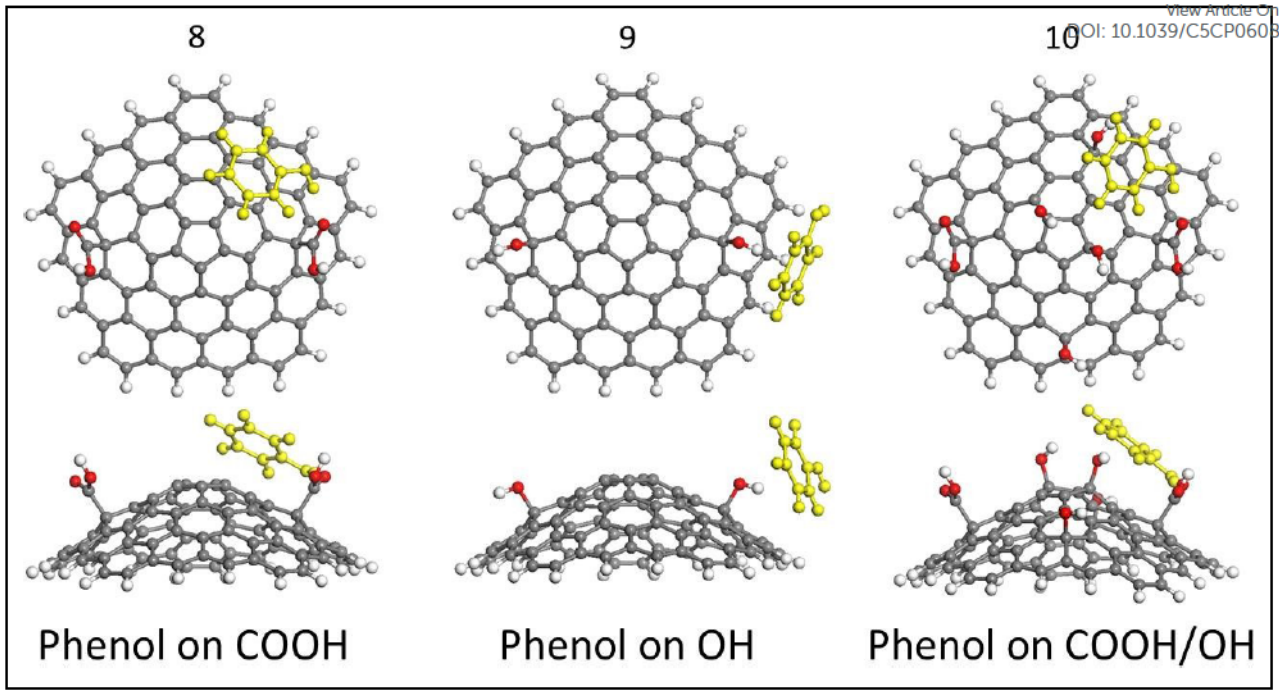

Figure 4. Optimized adsorption positions (top and side views) of phenol interacting directly with the functional groups (COOH and OH) on curved carbon sheet.